

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :	A1	(11) International Publication Number: WO 98/36434 (43) International Publication Date: 20 August 1998 (20.08.98)
(21) International Application Number: PCT/BE98/00019 (22) International Filing Date: 13 February 1998 (13.02.98) (30) Priority Data: 97870021.9 17 February 1997 (17.02.97) EP (34) Countries for which the regional or international application was filed: BE et al.		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(71) Applicant (for all designated States except US): MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MAY, Bronislav, Henri [BE/BE]; Courtenodreef 5, B-3090 Overijse (BE). MIONOTTE, Philippe, Gérard [BE/BE]; Rue Saint Martin 21, B-4217 Heron (BE). (74) Agent: BOSCH, Henry, A.; Monsanto Services International S.A./N.V., Avenue de Tervuren 270, B-1150 Brussels (BE).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
(54) Title: METHOD FOR THE MANUFACTURE OF PHOTOVOLTAIC CELL (57) Abstract		
<p>The technology of this invention relates to a commercially attractive manufacturing method for photoelectrochemical cells. In essence, a photovoltaic ink suspension, containing essentially nanocrystalline semi-conductor particles, a hydrolysable semi-conductor precursor alkoxide, a sensitizing dye and an inert solvent, is applied to a conductor area followed by in situ treatment of the ink to yield a semi-conductor effective layer for use in a photovoltaic cell. The components of the photovoltaic ink can be applied simultaneously or sequentially, provided the semi-conductor functional particles are applied first.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD FOR THE MANUFACTURE OF PHOTOVOLTAIC CELL

The technology of this patent application relates to a method for the manufacture of a photovoltaic cell which can be used for converting incident light into electrical energy. The method basically comprises applying a photovoltaic ink consisting essentially of a suspension of the dye-coated particles of the semi-conductor functional layer, a hydrolysable semi-conductor precursor, such as a hydrolysable metal alkoxide, and an inert, in relation to the metal alkoxide, solvent, is applied to a substrate provided with conductor patterns, to thereby generate under temperature conditions not exceeding 180 C°, a semi-conductor functional layer for use in a regenerative photovoltaic cell.

The prior art relating to regenerative photovoltaic cells is crowded and diverse and is possessed, in addition to detailed proposals concerning mechanisms underlying the conversion of light to electrical energy, of methods for the manufacture of such cells, particularly the semi-conductor functional part, which relays and regulates the transport of photoexcited electrons from the chromophore dye to the anode conductor. EP-A-0 333 641 describes photo-electrochemical cells having a polycrystalline metal oxide semi-conductor with a monomolecular chromophore layer in its surface region. At least one of the electrodes shall be transparent to the incident light. The cells are of the dual substrate "sandwich-type" configuration having oppositely charged current collectors attached to distinct substrates. The semi-conductor part is provided with sintered (electrically conductive) nano-cells, such as TiO₂. The cells are

made by depositing sequentially minimal amounts of semiconductor precursors followed by high temperature sintering after each deposition of precursor

Kavan et al., J. of The Electrochemical Society, February 1996, pages 394-400, have reported that sintering can reduce the (BET) surface area of nanocrystalline TiO_2 and henceforth its photoelectrochemical conversion functionality. Péchy et al., J. Chem. Soc., Chem. Commun., 1995, pages 65-66, describe the preparation of phosphonated polypyridyl ligands which are reported to exhibit excellent charge-transfer sensitizer properties for nanocrystalline TiO_2 film application. These characteristics render the phosphonated polypyridyl ligands particularly attractive for application in molecular photovoltaic devices.

Hanprasopwattana et al., Langmuir 1996, 12, 3173-3179, describe methods of uniformly distributing monolayer to multilayer films of titania on mono-disperse silica spheres. The titania coatings so deposited are amorphous. Heating to temperatures around 500°C is needed to convert the amorphous coating into polycrystalline TiO_2 . Kay et al., The Journal of Physical Chemistry 1996, Vol. 98, pages 952-959, report on the mechanism of photosensitization of transparent TiO_2 electrodes with chlorophyll derivatives, particularly induced photocurrent phenomena. Grätzel et al., Current Science, Vol. 66, No. 10, 25 May 1994, describe properties and requirements of efficient dye-sensitized photoelectrochemical cells for direct conversion of visible light to current. The authors conclude that actual cell technology (at the date of the paper) is not sufficient and cannot lead to commercially viable executions. McEvoy et al., Solar Energy Materials and Solar Cells 32 (1994) 221-227,

summarize general principles and the historical development sequence concerning photovoltaic technologies.

While substantial efforts were invested towards providing economically acceptable manufacturing technology for photo-electrochemical cells, these developments efforts have not yielded, as of yet, acceptable solutions, in particular meaningful improvements to current photovoltaic cell making technology.

It is therefore a main object of this invention to make available a simplified and reliable method for the manufacture of photovoltaic cells. It is a further object of this invention to generate a method for the manufacture of photovoltaic cells whereby the semi-conductor functional layer can be produced/deposited in a relatively simple arrangement without a need for using extreme, possibly repetitive, conditions such as sintering temperatures. It is still another object of this invention to provide a high speed, as compared to previous methods, manufacturing process for photovoltaic cells. Yet another object of this invention aims at economically producing semi-conductor functional layers for use in photovoltaic cells. It is still another object of this invention to provide a method for the manufacture of photovoltaic cells which does not require extreme conditions of temperature and/or elaborate control of the surrounding atmosphere. The foregoing and other objects of this invention can now be met beneficially with the aid of the manufacturing arrangement of this invention.

This invention, in part, relates to a method for the manufacture of regenerative photovoltaic cells containing

substrates, current collectors and dye-coated semi-conductor functional layer, wherein a photovoltaic ink consisting essentially of a suspension of agglomerates of the semi-conductor functional particles, a hydrolysable semi-conductor precursor, a sensitizing dye and an inert solvent, is applied to a conductor functional substrate e.g. a substrate provided with conductor patterns to thereby generate under temperature conditions not exceeding 180 °C, a semi-conductor functional layer.

The semi-conductor particle capable of exhibiting semi-conductor functionality can preferably be represented by nanocrystalline metal oxides of titanium, zirconium, hafnium, strontium, zinc, indium, tin, antimony, yttrium, lanthanum, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and mixtures of such metal oxides. The metal in the metal alkoxides can be selected from the preferred metals which can be used in the polycrystalline semi-conductor metal oxides. The ink can, in addition to the essential metal alkoxide, contain, as an optional ingredient, a non-semi-conductor metal, or non-metal, alkoxide selected from silicon, aluminum, germanium and boron in a level of from 0.1% to 20% expressed in relation to the essential metal alkoxide component (100%). The solvent is inert in relation to the metal alkoxide component. The photovoltaic ink is deposited onto the substrate to thus provide ohmic contact between the anode conductor and the photovoltaic layer. The ink can be applied to the conductor-substrate by methods generally known inclusive of printing and other deposition methods.

The terms "photovoltaic cell" and photoelectric cell are used interchangeably. Percent indications stand, unless specified differently, for "% by weight".

The method herein can serve for the manufacture of photovoltaic cells generally. Examples of such cells embrace conventional dual substrate "sandwich-type" cells as e.g. known from EP-A-0 333 641 and single substrate cells as e.g. known from EP-A-97870011.1, entitled "Photovoltaic Cell", filed January 30, 1997. Photovoltaic cells manufactured in accordance with the method herein generally comprise a substrate or substrates, current collectors and a semi-conductor functional layer resulting from the application of a photovoltaic ink to a substrate provided with conductor patterns to thereby generate under temperature conditions not exceeding 180 °C a semi-conductor functional layer.

The photovoltaic ink consists essentially of a suspension of agglomerates of the particles of the semi-conductor functional layer, a hydrolysable metal alkoxide, a sensitizing dye and an inert solvent. The suspension can be a physical mixture of all the essential ingredients or a mixture of two or more of them, with the proviso that the semiconductor nanoparticles and a liquid vehicle are always components of the suspension. The liquid vehicle can be represented by any suitable and compatible/non-reactive compound or mixture of such compounds. As an example, the liquid vehicle can be represented by the inert solvent. The suspension has to be stable i.e. the particles should not settle or otherwise precipitate from the suspension within the time period generally required for the application. The suspension shall be stable, under ambient

conditions of temperature, pressure and humidity, for a period of, at least, one hour, preferably at least 4 hours, more preferably at least one week.

The suspension shall have a viscosity that is compatible with the particulars of the selected application, usually printing, such as screen printing, or deposition by means of adequate tools including roll deposition or doctor-blading. The viscosity will vary depending upon the level and the particle size of the dye-coated metal oxide particles. The presence of optional performance additives in the ink can also affect, possibly in a significant manner, the viscosity. The viscosity of the photovoltaic ink herein is generally within the range of from 1 to 100 000 P (Poises), frequently within the range of from 100 to 40 000 P. The viscosity of any given ink can be adjusted thereby taking into consideration the particular requirements, generally known in the relevant domain, of the selected method of application. The viscosity is measured under standard conditions at a temperature of 25 (+/-2) °C. While the ink, in a concentrated form, can contain up to 50% of the coated metal oxide particles, these particles usually represent from 5% to 35%, preferably from 8% to 25%, more preferably from 8% to 18%, expressed in relation to the sum of dye-coated metal oxide particles + hydrolysable metal oxide + solvent (100%)

The photoactive particles can be represented by nanocrystalline metal oxide particles, capable of exhibiting, within the framework of the photovoltaic cell herein, effective semiconductor properties. The metal component of the nanocrystalline oxide particles can be selected from transition metals, or from elements selected from the fourth, fifth or sixth group or sub-

group of the periodic system of elements, in particular titanium, zirconium, hafnium, strontium, zinc, indium, tin, antimony, yttrium, lanthanum, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, or mixtures of two or more of these metal oxides. The nanocrystalline metal oxide particles, having semi-conductor properties, are coated with a monomolecular layer of a chromophore capable of ejecting an electron upon exposure to incident light which electron will be relayed by the semi-conductor to the conductor. The metal oxide particles have an average particle diameter of from 1 nm to 200 nms, preferably from 10 nms to 50 nms. The metal oxide particles can, and frequently do, form agglomerates having a diameter in the range of from 100 nms to 1 mm.

The nanocrystalline metal oxide particles can be prepared by methods generally known in the art. For example, the particles can be prepared by hydrolysis of the corresponding metal (or metalloid) alkoxides, chlorides or bromides followed by optional physical treatments such as growth and particle size control through digestion under hydrothermal conditions at temperatures in the range of from 150 to 250 °C. The chromophore dye will be applied, before, simultaneously or preferably after deposition of the ink, to the particulate metal-oxide by soaking or spraying an aqueous solution, or more preferably an organic solvent solution thereof. The excess dye (not adsorbed or chemisorbed or otherwise reacted with the semi-conductor surface) can be rinsed off. Chromophore dyes which can be used in connection with the cell manufactured in accordance with the method herein are eminently well known in the technical community. Examples of suitable chromophore dyes for use in this invention are disclosed in EP-A-97870011.1, page 7, lines

16-29. The dye can optionally be used under polymeric form i.e. included as pendant groups or as monomeric units in a polymer chain to thus improve the stability of the chromophore layer. Examples of the chromophore dye in polymeric configuration for use herein are described in JP-A-85196467 to Rykagaku Kenkyusho.

The hydrolysable semi-conductor precursor is usually represented by hydrolysable metal alkoxides wherein the metal moiety is selected among the metals of the inventive nanocrystalline metal oxides exhibiting semi-conductor functionality. Preferred metals, for use in the hydrolysable alkoxides herein, belong to groups IIb, IVb, Vb, VIb, IIIa, IVa and Va of the Mendeleev table of elements. The preparation of the alkoxides is well known in the technical community. In fact, the majority, if not all, of the metal alkoxides for use herein are known and commercially available materials. The alkoxide moiety can be represented by species having, for example, from 1-10 carbon atoms. Specific examples of the like alkoxides include methoxide, ethoxide, propoxide, isopropoxide, butoxide a.s.o. The hydrolysable metal alkoxides, which correspond to the hydrolysable semi-conductor precursor, are generally employed in levels ranging from 0.1% to 15%, preferably 0.2% to 10%, expressed on the same basis as the metal oxide particles. In a preferred embodiment, it can be beneficial to incorporate, in addition to the hydrolysable semi-conductor precursor, a low level such as from 10⁻⁶% to 10%, expressed in relation to the hydrolysable semi-precursor metal alkoxide (100%), of a further (non semi-conductor) metal alkoxide selected from silicon, aluminum, germanium, and boron.

The inert solvent is generally used in levels ranging from 6% to

85%, preferably from 10% to 80%, expressed on the same level as the metal oxide particles. The term inert means that the solvent is not capable of reacting with the other components present in the ink suspension, under ambient (20 °C) storage conditions for a period of 6 months. Examples of suitable solvents include straight and branched alkanes having from 8 to 20 carbon atoms, aromatic alkylates having from 4 to 12 carbon atoms in the straight or branched alkyl chain, ethers or ketones having from 8 to 24 carbon atoms and blends thereof.

The ink suspension can further contain additive levels i.e. 0.1% to 2.0%, of various optional performance and compatibilizing agents which are used for their known functionality. Such additives can serve to enhance the functionality of any one of the essential ternary ingredients in the ink suspension. Examples of the like additives can be represented by printing binders which can enhance the even distribution of the ink particles on the substrate.

The suspension shall be distributed onto the conductive substrate or substrate provided with conductive patterns by methods generally known inclusive of printing, roll deposition or doctor blading to thereby yield a level of precursor ink in aleatory electrical contact with the underlying conductor arrangement. The so deposited layer of the ink will be treated under mild and non-destructive conditions including temperatures below 180 °C, preferably below 150 °C, possibly combined with non destructive pressures e.g. below 20 bars, and/or evaporation under subatmospheric pressures. So proceeding will yield an effective semi-conductor functional grid which can control and promote the transport of electrons originating from the

chromophore dye to the conductive layer. The actual and combined optimization of physical conditions required for converting the ink suspension into an effective semi-conductor grid are routine measures. In a preferred execution, the support of the deposited layer has a resistance equal to or less than 10 ohms square to achieve an appropriate and beneficial level of photochemical performance.

In a preferred embodiment, the core of the aggregates of the semi-conductor particles can be represented by inactive metal oxides particles such as alumina and silica provided, of course, that such inactive core is coated with a semi-conductor functional layer comprising a metal oxide semi-conductor wherein the metal is selected from titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chrome cadmium, antimony, tin, molybdenum, tungsten and mixtures of two or more of these metal oxides. The term "inactive" as used in that context means that the particular metal oxide e.g. silica and/or alumina does not exhibit semi-conductor properties upon use in a photovoltaic cell manufactured in accordance with the method of this invention. The from a semi-conductor standpoint inactive core can represent up to 80%, preferably up to 60% of the aggregates of dye-coated particles.

The substrate for use in the cell manufactured in accordance with this invention can be represented by conventional substrate materials. Such materials can be selected from flexible or rigid, mineral or organic materials, such as synthetic and natural polymers, glass, carbon, conductive metals such as

titanium, tantalum, molybdenum, stainless steel (302; 304; 316; 321; 310; 17-7PH), Hastelloy C-276, tungsten, inconel, zirconium and comparable metals or metal alloys or combinations thereof well-known in the relevant domain. The terms stainless steel (302; 304; 316; 321; 310; 17-7PH), Hastelloy C-276 and inconel have the meaning given in PERRY'S CHEMICAL ENGINEERINGS' HANDBOOK, 6th Edition, R.H. Perry, D.W. Green, J.O. Maloney, McGraw Hill Book Company, 1984.

In another execution of the cell made by the method herein, a minor proportion of semi-conductor particles is embedded into the anode conductor. Preferably from 1% to 10% by weight, expressed versus the conductive material (100%), of the said semi-conductor particles are embedded into the conductive material layer. In another execution herein, the anode conductor is provided with a supplementary layer of semi-conductor metal oxides before applying the photovoltaic ink. This supplementary layer is deposited by known means and is electronically interconnected with the anode conductor.

The photovoltaic cells manufactured in accordance with the method of this invention can be used beneficially for converting incident light into electrical energy. Visible light generally having a wave-length in the range of from 300 nms to 900 nms (nms = nanometers), preferably daylight having a wave-length in the range of from 400 nms to 700 nms are for obvious reasons prime sources of light. It is understood, however, that the cell in accordance with this invention can be manufactured and correspondingly optimized with whatever source of light energy is available.

Example 1:

A photovoltaic ink was prepared as follows : 15 g of titanium dioxide particles (mainly Anatase, DEGUSSA P 25TM) were ground in a mortar with 100 ml of a 3 mmolar solution of Ru L₂ (SCN)₂ (L = 4,4'-dicarboxy-2,2'-bipyridyl) in ethoxyethanol containing 15 mmol of titanium tetra-isopropoxide/liter (Aldrich) . The operation was conducted in a dry box to protect the isopropoxide from atmospheric moisture . The dyed titanium oxide powder was dried under vacuum and stored in the dark. To prepare the dye-coated titanium dioxide ink, 3 g of the above powder were ground in a mortar with a minimum amount of ethoxyethanol (approximately 3 g), added gradually until the resulting ink paste acquired a viscosity compatible with the chosen deposition technique.

A photoactive electrode was prepared from the above ink as follows : a 3 cm X 2 cm piece of fluorine doped tin oxide coated glass (Libby-Owens-Ford - conductivity 8 Ohm square) was partly coated on the conductive side with the dye coated titanium dioxide ink (ink film thickness approximately 30 micrometers, the coated area was 0.5 X 0.5 cm in the middle of the plate). The electrode was allowed to dry at room temperature in the dark for two hours.

A photovoltaic cell was assembled using the above electrode and a counter electrode made by spraying a similar piece of the same doped tin oxide coated glass with a fine mist of hexachloroplatinic acid in isopropanol, at a 5 mmolar concentration, followed by heating at 390 C for 30 minutes. The two electrodes were disposed face-to-face, and the edges of the assembly were sealed with a hot pressed thin (1.5 mil) polyethylene gasket (Surlyn TM). A regenerative electrolyte, consisting of a 0.3 molar lithium iodide and 0.03 molar iodine solution in 25 % volume N-methyl pyrrolidinone/ 75 % volume acetonitrile, was admitted by capillarity between the electrodes .

The cell was irradiated with a 500 watt bulb at a distance sufficient to produce a response equivalent to one sun on a calibrated silicon solar cell (Edmunds Scientific). An ammeter was connected across the two electrodes : a short circuit current of 0.275 mA/cm² and an open circuit voltage of 530 mV were measured.

Example 2 :

A two component ink was prepared as follows.

The first ink component was prepared as follows: 15 g of TiO₂ (DEGUSSA P 25 TM), 7.5 ml of distilled water and 1 drop of concentrated nitric acid were ground together in a mortar.

7.5 ml of ethoxyethanol were gradually added, under continued grinding, until the viscosity of the resulting ink paste was adequate for the chosen deposition method. The second ink component was prepared by adding 0.43 g (1.5 mmole) of titanium tetra isopropoxide (Aldrich) to 100 ml of a 0.3 mmolar solution of Ru L₂ (SCN)₂ (L = 4,4'-dicarboxy-2,2'-bipyridyl) in dry ethoxyethanol.

The first ink component (Titanium dioxide slurry) was deposited on conductive glass as described in Example 1. The coated glass plate was dried for 1 hour at 150 °C in an oven, cooled down and placed in a dry glove box to protect it from atmospheric moisture. A small amount (two drops) of the second ink component was deposited onto the dried TiO₂ film and the solvent allowed to evaporate. The latter operation was repeated 3 times, until a sufficient amount of reactive dye had been adsorbed onto the titanium dioxide film. The coated glass plate was exposed to ambient air for 10 minutes in the dark, then mounted into a photovoltaic cell according to Example 1, except that the electrolyte solution solvent was 3-methoxypropionitrile, instead of a mixture of acetonitrile and N-methylpyrrolidinone.

The cell was irradiated with a 500 watt bulb at a distance sufficient to produce a response equivalent to one-tenth of a sun on a calibrated silicon solar cell (Edmunds Scientific). An ammeter was connected across the two electrodes : a short

circuit current of 0.05 mA/cm² and an open circuit voltage of 470 mV were measured.

Example 3:

The titanium dioxide slurry of Example 2 was deposited onto conductive glass as described in Example 1. After drying at 150 °C, a small amount (1 drop) of a 300 mmolar solution of titanium tetra-isopropoxide in dry isopropanol was deposited onto the dried TiO₂ film and the solvent allowed to evaporate under ambient conditions. The glass plate was then soaked overnight in 5 ml of 0.3 mmolar Ru L₂ (SCN)₂ (L = 4,4'-dicarboxy-2,2'-bipyridyl) in ethanol. The coated glass plate was mounted as the photoactive electrode in a photovoltaic cell according to Example 1.

The cell was irradiated with a 500 watt bulb at a distance sufficient to produce a response equivalent to one sun on a calibrated silicon solar cell (Edmunds Scientific). An ammeter was connected across the two electrodes : a short circuit current of 5.49 mA/cm² and an open circuit voltage of 602 mV were measured.

Example 4:

A titanium dioxide slurry was prepared in a mortar from 20 g

of DEGUSSA P 25™ titanium dioxide powder, 80 ml of distilled water and enough concentrated nitric acid to bring the pH of the resulting suspension to 2. A 316 stainless steel gauze (50 mesh, wire thickness 0.25 mm) was carefully degreased and cleaned in hot water containing a trace of a commercial surfactant (Triton™), dipped into the suspension, dried first in air at room temperature, then in an oven at 130 °C. The operation was repeated two times. The TiO₂ coated gauze was impregnated with a few drops of a 0.2 molar solution of titanium isopropoxide in ethanol. It was dried again as above and placed overnight in 10 ml of 0.3 mmolar Ru L₂ (SCN)₂ (L = 4,4'-dicarboxy-2,2'-bipyridyl) in ethanol.

A photovoltaic cell was assembled, using the above gauze as the active photoelectrode, sandwiched with a conductive glass platinized counter electrode according to Example 1. The two electrodes were placed in a sealed "envelope" consisting of two sheets of polyethylene terephthalate and a seal of cured room-temperature-vulcanisable silicone adhesive. The cell was filled with electrolyte solution as per Example 2, using a syringe inserted through the silicone sealant.

The cell was irradiated with a 500 watt bulb at a distance sufficient to produce a response equivalent to one-tenth of a sun on a calibrated silicon solar cell (Edmunds Scientific). An ammeter was connected across the two electrodes : a short circuit current of 0.13 mA/cm² and an open circuit voltage of

410 mV were measured.

CLAIMS

1. A method for the manufacture of photovoltaic cell containing a substrate, current collectors, dye-coated semi-conductor functional layer wherein a photovoltaic ink consisting essentially of a suspension of the nanocrystalline particles of the semi-conductor functional layer, a hydrolysable semi-conductor precursor, such as a hydrolysable metal alkoxide, a sensitizing dye and an inert solvent, is applied to a substrate provided with conductor patterns to thereby generate, under temperature conditions not exceeding 180 °C, a semi-conductor functional layer.

2. The method in accordance with Claim 1 wherein the components of the photovoltaic ink are sequentially deposited onto the substrate whereby the particles of the semi-conductor functional layer, in combination with a liquid vehicle, are deposited first.

3. The method in accordance with Claim 1 wherein the metal in the metal alkoxide is selected from titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chrome, cadmium, antimony, tin, molybdenum and tungsten or mixtures of these metal alkoxides.

4. The method in accordance with Claim 3 wherein, in addition, a further metal alkoxide is present selected from silicon, aluminum, germanium and boron in a level of from 10⁻⁶% to 10%, expressed in relation to the metal alkoxide

(100%).

5. The method in accordance with Claims 1 or 2 wherein the particle is represented by inert, photochemically and electrically inactive within the context of this method, material, such as silica or alumina, coated with a semiconductor functional layer comprising a metal oxide semiconductor wherein the metal is selected from titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chrome, cadmium, antimony, tin, molybdenum and tungsten or mixtures of these metals.

6. The method in accordance with Claims 1 or 2 wherein the substrate is selected from flexible or rigid, mineral or organic materials, such as synthetic and natural polymers, glass, carbon, conductive metals such as titanium, tantalum, molybdenum, stainless steel (302; 304; 316; 321; 310; 17-7PH), Hastelloy C-276, tungsten, inconel, zirconium and comparable metals or metal alloys or combinations thereof.

7. The method according to Claims 1 or 2 wherein the photovoltaic ink is deposited onto the substrate containing anode and cathode conductors to provide ohmic contact between the photovoltaic layer and the anode conductor to thus yield a single substrate cell or on an individual substrate provided with anode conductor to thus yield, in combination with another substrate provided with the cathode conductor, a sandwich-type cell.

8. The method according to Claim 7 wherein the anode conductor is provided with a supplementary layer of semiconductor oxides before applying the photovoltaic ink.

9. The method according to Claim 7 wherein the anode conductor contains from 1% to 10% by weight, expressed versus the conductive material (100%), of semi-conductor metal oxide particles.

INTERNATIONAL SEARCH REPORT

Inte
ional Application No
PCT/BE 98/00019

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 42 25 575 A (ABB PATENT GMBH) 10 February 1994 see column 1, line 60 - column 2, line 45 ----	1-3,6,7
A	DE 44 21 978 A (PENTH BERND DR) 4 January 1996 see column 3, line 65 - column 4, line 33 -----	1-3,6,7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 June 1998	17/06/1998
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentdaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx: 31 651 epo nl, Fax: (+31-70) 340-3016	Schuermans, N

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte	onal Application No
	PCT/BE 98/00019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4225575 A	10-02-1994	EP 0582212 A JP 6188446 A US 5362514 A	09-02-1994 08-07-1994 08-11-1994
DE 4421978 A	04-01-1996	DE 4437767 A DE 4439722 A WO 9600198 A EP 0766657 A	25-04-1996 15-05-1996 04-01-1996 09-04-1997